



Development of highly efficient sulfur-doped TiO₂ photocatalysts hybridized with graphitic carbon nitride



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ABSTRACT

Graphitic carbon nitride (g-C₃N₄) has attracted much attention as a metal-free semiconductor having visible-light absorption and relatively high chemical stability. In the present study, we hybridized g-C₃N₄ with sulfur-doped TiO₂, which is a visible light-responsive photocatalyst with high oxidation ability, in order to improve photocatalytic activity under visible-light irradiation. Hybrid photocatalysts were prepared by three methods: agate mortar, sonication, and planetary mill. Activities of the hybrid photocatalysts depended on the mixing method. The sample prepared by a planetary mill showed the highest photocatalytic activity, 4-times higher than that of sulfur-doped TiO₂. We concluded that the high activity of the hybridized sample under visible-light irradiation is induced by charge transfer between the two photocatalysts mimicking the Z-scheme in photosynthesis.

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1. Introduction

Clean technology utilizing the sunlight and artificial light around us has been attracting much attention in recent years due to concerns about environmental issues, and it has been expanding rapidly worldwide. Photocatalysts have been studied as a means to utilize the abundant light. Titanium(IV) oxide (TiO₂) has been one of the most attractive materials as a photocatalyst owing to its nontoxicity, availability, superior redox ability, and photostability [1]. However, TiO₂ has a bandgap of 3.0–3.2 eV, and ultraviolet (UV) light is vital to its photocatalytic reaction. Therefore, many attempts have been made to design highly active TiO₂ under visible-light excitation for utilization of sunlight and indoor light illumination. The most widely used method for this has been impurity doping in TiO₂ since the report by Asahi et al. of anionic nitrogen-doped TiO₂ having photoabsorption and photocatalytic activity under visible-light irradiation [2]. However, visible-light activity of doped TiO₂ has been still low compared to the activity of TiO₂ under UV light irradiation. One possible reason for the low activity is increase in recombination centers and trapping sites produced by impurity doping.

Here, we focused on a hybrid of two semiconductors to improve photocatalytic activity under visible-light irradiation. Some studies using a charge separation model [3–6] or Z-scheme model [7–9] have suggested that charge transfer proceeds at the interface between two semiconductors in a hybrid photocatalyst, resulting in increase in photocatalytic activity. In the case of doped TiO₂, a combination pair that acts as reduction part of the semiconductor with high reductive potential in the Z-scheme model is ideal because most of the doped TiO₂ has difficulty in reduction reaction rather than oxidation reaction.

Recently, graphitic carbon nitride (g-C₃N₄), which is an organic semiconductor with visible-light absorption and high reduction ability, has attracted much attention since it can produce hydrogen from water under visible-light irradiation in the presence of a sacrificial donor [10]. The bandgap and flat-band potential of g-C₃N₄ were reported to be 2.67 eV and −1.42 V (versus Ag/AgCl, pH 6.6) from estimation by (αhν)² versus photon-energy plots and Mott-Schottky plots, respectively [11]. Thus, g-C₃N₄ has superior reduction ability due to the high potential of the conduction band, though its oxidation ability is inferior. Moreover, g-C₃N₄ can be synthesized by a simple and low-cost route, and it has relatively good stability under light irradiation in a water solution as well as in acid or base solutions due to the strong covalent bonds between carbon and nitride atoms [12].

In this study, we hybridized g-C₃N₄ with cationic sulfur-doped TiO₂ (S-TiO₂). S-TiO₂ has been shown to exhibit visible-light absorption, which is attributed to the formation of an electron-occupied level above the valence band consisting of S 3s states,

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Table 1

S_{BET} , R_{PL} and photocatalytic activity of the prepared samples. R_{PL} is intensity ratio of the PL peak attributed to radiative recombination of p-g-C₃N₄ under excitation at the wavelength of 350 to that of 420 nm.

Name	Sample	Treatment	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	R_{PL}	CO ₂ evolution for 24 h/ppmv
TiO ₂	TiO ₂	No treatment	62	–	21
S-TiO ₂	S-TiO ₂	No treatment	60	–	150
p-S-TiO ₂	S-TiO ₂	Planetary mill	59	–	278
g-C ₃ N ₄	g-C ₃ N ₄	No treatment	10	–	67
p-g-C ₃ N ₄	g-C ₃ N ₄	Planetary mill	21	0.76	257
a-SC	S-TiO ₂ , g-C ₃ N ₄	Agate mortar	43	–	240
s-SC	S-TiO ₂ , g-C ₃ N ₄	Sonication	45	–	163
p-SC	S-TiO ₂ , g-C ₃ N ₄	Planetary mill	63	0.70	708
p-TC	TiO ₂ , g-C ₃ N ₄	Planetary mill	48	0.77	182
a-SpC	S-TiO ₂ , p-g-C ₃ N ₄	Agate mortar	55	0.84	162
a-pSpC	p-S-TiO ₂ , p-g-C ₃ N ₄	Agate mortar	–	–	210

and to exhibit photocatalytic activity under visible light with wavelengths up to 550 nm [13]. Recently, there have been several reports on hybrids of g-C₃N₄ with TiO₂ [14], TaON [15], and poly(3-hexylthiophene) [16]. However, a charge separation mechanism was employed in these photocatalysts, and explanation of the mechanism was not sufficient. In the present study, we also elucidated the reaction mechanism of the hybrid photocatalyst by using PL measurement and action spectrum analysis.

2. Experimental

2.1. Materials

g-C₃N₄ powders were prepared by heat treatment of melamine (Wako Pure Chemical Industries, Ltd., 99%). 30 g of melamine in an alumina pot was heated at 550 °C for 4 h with a temperature rise rate of ca. 9 °C min^{−1} in a muffle furnace. S-TiO₂ powders were commercial samples (Toho Titanium Co. Ltd., GPP8Y01) containing 0.04 wt% sulfur. The crystal structure of S-TiO₂ powder was anatase without any other crystal phase. Commercially available anatase TiO₂ (Ishihara Sangyo Co. LTD., ST-21) was used as a reference.

2.2. Preparation of hybrid photocatalysts

S-TiO₂ and g-C₃N₄ were hybridized in the ratio of 2:1 (wt:wt) by three methods, i.e., agate mortar method, sonication method and planetary mill method. For the agate mortar method, two kinds of powder were ground by an agate mortar for ca. 15 min. For the sonication method, two kinds of powder were suspended in 20 ml of ion-exchanged water by sonication for 30 min followed by stirring for 3 h. Then the sample was separated by filtration, washed with water several times, and dried in a vacuum drying oven at 60 °C overnight. For the planetary mill method, 1.5 g of two kinds of powder and 20 ml of ion-exchanged water were added to a 50 mL agate bowl containing 50 g of yttrium-stabilized zirconia grinding beads (NIKKATO Co. Ltd., $\Phi = 0.6$ mm). Then the agate bowl was put on planetary mill (Fritsch Japan Co. Ltd., Planetary Micro Mill pulverisette 7) and the planetary mill was operated at 750 rpm for 10 min. After removing the beads by screening, the sample was separated by filtration, washed with water several times, and dried in a vacuum drying oven at 60 °C overnight. Samples names and the hybrid methods are summarized in Table 1.

2.3. Characterization of prepared samples

Crystal structures of the particles were confirmed by using an X-ray diffractometer (Rigaku, MiniFlex II) with Cu K α radiation ($\lambda = 1.5405$ Å). Functional group vibrations were confirmed by using a Fourier transform infrared spectrometer (FTIR; ASCO,

4200ST) with a diffuse reflectance accessory (JASCO, DR-81). Diffuse reflectance spectra were measured using a UV–vis spectrophotometer (Shimadzu, UV-2600) equipped with an integrating sphere unit (Shimadzu, ISR-2600). The specific surface area (S_{BET}) of the particles was measured by nitrogen adsorption on the basis of the Brunauer–Emmett–Teller equation with a surface area analyzer (Quantachrome, Nova 4200e). The morphology of prepared particles was observed by a scanning electron microscope (SEM; JEOL, JSM-6701FONO). Fluorescence spectra were obtained using a photoluminescence (PL) spectrometer (HITACHI, F-2500).

2.4. Photocatalytic activities

Photocatalytic activities of samples were evaluated by photocatalytic decomposition of acetaldehyde. Two hundred milligrams of powder, which has complete extinction of incident radiation, was spread on a glass dish, and the glass dish was placed in a 125 cm³ Tedlar bag (Polyvinyl fluoride, AS ONE Co. Ltd.), and then the Tedlar bag was sealed by laminating. Five hundred parts per million by volume of gaseous acetaldehyde was injected into the Tedlar bag, and photoirradiation was performed at room temperature after the acetaldehyde had reached an adsorption equilibrium (after 2 h). In order to estimate dark adsorption ability of the photocatalysts, concentration of acetaldehyde under the absorption equilibrium in the dark was measured. The gaseous composition in the Tedlar bag was 79% N₂, 21% O₂, <0.1 ppmv of CO₂ and 500 ppmv of acetaldehyde, and relative humidity was ca. 30%. A 500-W xenon lamp (Ushio, SX-UI501XQ) was used as a light source and the wavelength of photoirradiation was controlled by L-42 filters ($\lambda > \text{ca. } 400$ nm, Asahi Techno Glass Co.) with an intensity

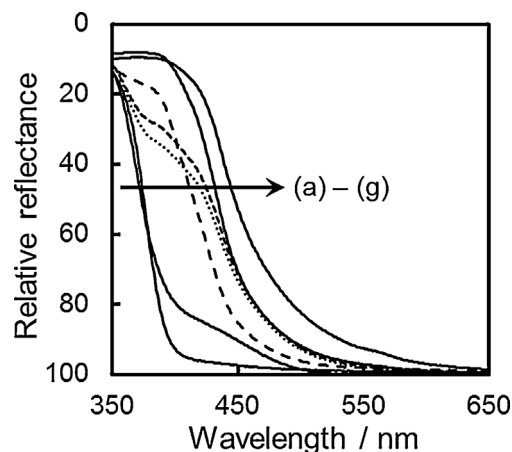


Fig. 1. Diffuse reflectance spectra of (a) TiO₂, (b) S-TiO₂, (c) p-SC, (d) a-SC, (e) s-SC, (f) p-g-C₃N₄ and (g) g-C₃N₄.

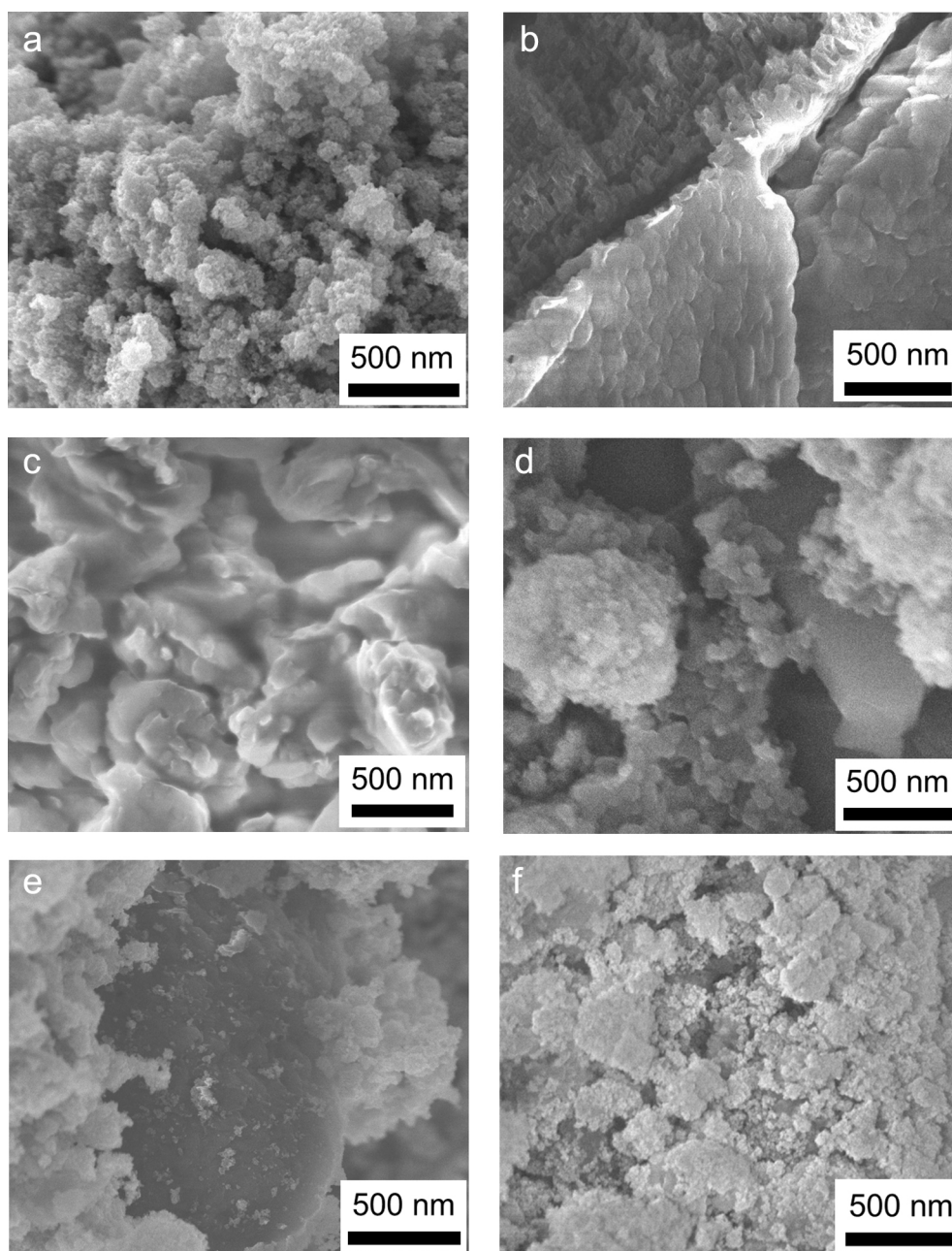


Fig. 2. SEM images of (a) S-TiO₂, (b) g-C₃N₄, (c) p-g-C₃N₄, (d) a-SC, (e) s-SC and (f) p-SC.

of 12 mW cm⁻² being used as the light source. For measurement of action spectra, light-emitting diodes (Nichia NCCU033B, Epitex L415-66-60, Epitex L435-30M32L, Lumileds LXHL-LR3 C, Lumileds LXHL-LB3 C, Lumileds LHL-NE98 and Lumileds LXHL-MM1D), which emitted light at wavelengths of ca. 365 nm, 415 nm, 435 nm, 455 nm, 470 nm, 505 nm and 530 nm, respectively, were used. The concentrations of acetaldehyde and carbon dioxide (CO₂) were estimated by gas chromatography (Agilent Technologies, 3000A Micro GC, TCD detector) with OV1 and PLOT-Q columns. The apparent quantum efficiency (QE) was defined by the following equation because of the 5-hole process for CO₂ production.

$$\begin{aligned} \text{QE} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number evolved CO}_2 \text{ molecules} \times 5}{\text{number incident photons}} \times 100 \end{aligned}$$

3. Results and discussion

3.1. Characterization

XRD patterns of the prepared g-C₃N₄ showed the strongest peak at 27.4°, which is attributed to stacking of aromatic systems for graphitic materials, and a weak peak at 13.0° (data not shown). In FTIR spectra of the prepared g-C₃N₄, characteristic stretching vibration of aromatic CN heterocycles in the region of 1200–1700 cm⁻¹ and breathing mode of the triazine units in the region of 810–900 cm⁻¹ were observed (data not shown). These results are similar to results of previously studies [13,17]. Therefore, it is thought that g-C₃N₄ was obtained from the heat treatment of melamine.

Fig. 1 shows diffuse reflectance spectra of prepared samples. S-TiO₂ and g-C₃N₄ exhibited visible-light absorption, and their

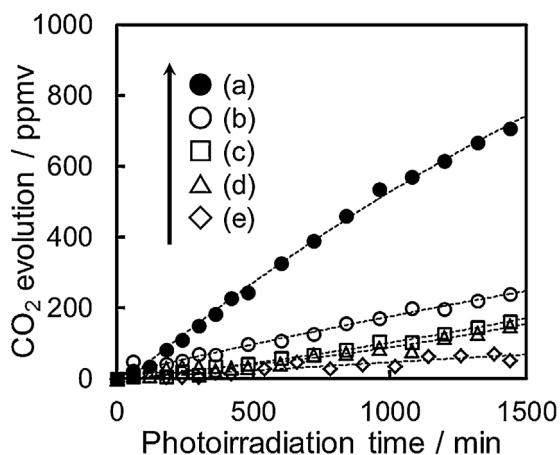


Fig. 3. Time courses of CO₂ evolution from acetaldehyde decomposition over (a) p-SC, (b) a-SCr (c) s-SC, (d) S-TiO₂ and (e) g-C₃N₄ under visible-light irradiation.

absorption edges were around 510 nm and 650 nm, respectively. The absorption spectrum of p-g-C₃N₄ was blue-shifted in comparison with that of g-C₃N₄. Ming et al. reported that the absorption spectrum of g-C₃N₄ was blue-shifted by ball mill treatment due to a decrease in particle size [18]. Similarly, in the case of p-g-C₃N₄, planetary mill treatment induced a decrease in particle size of g-C₃N₄, resulting in a blue shift of the absorption spectrum. On the other hand, the absorption spectrum of S-TiO₂ was not changed by planetary mill treatment (data not shown).

Fig. 2 shows the SEM micrographs of morphologies of hybrid photocatalysts. S-TiO₂ showed aggregated particles with particle size of several tens of nanometers (Fig. 2a), while g-C₃N₄ showed plate-like particles (Fig. 2b). By treatment with the planetary mill, g-C₃N₄ plate-like particles were pulverized into small particles (Fig. 2c). This agreed with two-fold increase in S_{BET} (Table 1). On the other hand, the morphology (data not shown) and S_{BET} of S-TiO₂ particles were not changed by planetary mill treatment (Table 1). In the sample prepared by the agate mortar and sonication method (a-SC and s-SC), two obviously different morphologies of particles were observed, and agglomerated S-TiO₂ particles were attached on plate-like g-C₃N₄ (Fig. 2d and e). In contrast, there was almost no difference in the morphologies of S-TiO₂ and g-C₃N₄ in the sample prepared by planetary mill method (p-SC) and it seemed that dispersed S-TiO₂ was covered on g-C₃N₄ particles (Fig. 2f). This indicates that g-C₃N₄ was pulverized into smaller particle even in the presence of S-TiO₂ and that dispersed S-TiO₂ particles attached to pulverized g-C₃N₄ particles before being aggregated. Very strong mechanical energy produced by a large amount of beads rotated at high speed may cause a chemical reaction on the surfaces of S-TiO₂ and g-C₃N₄ particles.

3.2. Photocatalytic activity

Fig. 3 shows time courses of CO₂ evolution for acetaldehyde decomposition over the prepared samples under visible-light irradiation. All of the hybrid photocatalysts showed higher activity than those of original S-TiO₂ and g-C₃N₄. This synergistic effect between S-TiO₂ and g-C₃N₄ implies that the mechanism mentioned in the introduction proceeded over the hybrid photocatalysts. The p-SC sample showed the highest activity, 4-times higher than those of the original samples in comparison of CO₂ evolution after 24 h of photoirradiation. Although p-SC showed the smallest visible-light absorption among the hybrid photocatalysts with different mixing methods (Fig. 1c–e), it showed the highest activity.

One plausible reason for this is the large S_{BET} of p-SC compared to those of samples prepared by other methods. Actually, g-C₃N₄

after planetary mill treatment (p-g-C₃N₄) showed a higher activity than that of original g-C₃N₄ because of an increase in S_{BET} . Moreover, S-TiO₂ after planetary mill treatment (p-S-TiO₂) showed a higher activity than that of original S-TiO₂. Judging from similar values to these S_{BET} , higher activity of p-S-TiO₂ is attributable to the change of condensed state of S-TiO₂ by planetary mill treatment without decreases in particle size. Thus, this induced high dispersion of S-TiO₂ particles, which provide superior adsorption and reactive sites for decomposition of acetaldehyde. However, the p-g-C₃N₄ hybridized with S-TiO₂ or p-S-TiO₂ using an agate mortar (a-SPC or a-pSPC) showed a much lower photocatalytic activity than that of p-SC (Table 1). Therefore, the large S_{BET} attributed to pulverization of g-C₃N₄ or condensed state of S-TiO₂ was not main reason for the high activity of p-SC. Another plausible reason is a large number of contact points between the two semiconductors as observed in SEM images of p-SC (Fig. 2f), compared to those for a-SC and s-SC (Fig. 2d and e). Thus, a large number of contact points induced smooth interfacial charge transfer of electrons and positive holes, resulting in separation of electron–hole pairs. A detailed discussion of the mechanism is given in the following section.

Photocatalytic activities of samples prepared by the three mixing methods in another mixing ratio of S-TiO₂ to g-C₃N₄ were also evaluated. As a result, samples hybridized in the ratio of S-TiO₂:g-C₃N₄ = 2:1 showed the highest activities, and we considered this ratio to be the optimum mixing ratio for S-TiO₂ and g-C₃N₄.

3.3. PL measurements

In order to confirm that the synergistic effect is due to charge transfer between the two semiconductors, PL measurements were carried out. It has been reported that g-C₃N₄ emits strong PL around 460 nm and that its spectrum depends on the degree of condensation and packing between the layers [19,20]. Actually, a PL spectrum with a peak wavelength of ca. 460 nm was observed under an excitation wavelength at 330 nm, and it was attributed to bandgap emission, judging from the optical bandgap of 2.7 eV evaluated by a diffuse reflectance spectrum (Fig. 1g). Similarly, strong PL emission of p-g-C₃N₄ was observed, but the PL spectrum with a peak wavelength of ca. 450 nm was blue-shifted by 10 nm from that of pure g-C₃N₄ [18]. This was due to a blue shift of absorption spectra of g-C₃N₄ as a result of decrease in particle size induced by planetary mill treatment (Fig. 1f and g). Although S-TiO₂ emits weak PL around 450 nm, its intensity was less than 5% of p-g-C₃N₄. Therefore, PL spectra of the hybridized samples were mainly determined by radiative recombination of electron–hole pairs in g-C₃N₄.

Fig. 4 shows PL spectra of p-TC and p-SC under excitation wavelengths at (a) 350 nm and (b) 420 nm. The peak wavelength in PL spectra of p-TC and p-SC was 450 nm, which corresponded to that of p-g-C₃N₄. p-SC showed the same PL spectrum as that of p-TC under excitation at the wavelength of 350 nm (Fig. 4a), while the PL peak intensity of p-SC was smaller than that of p-TC under excitation at the wavelength of 420 nm (Fig. 4b). However, an appreciable difference in morphology of these samples was not observed. Thus, these results suggest that visible-light absorption of S-TiO₂ decreased PL peak intensity because ST-21 does not have absorption in the visible-light region (Fig. 1a and b). This decrease in PL peak intensity is presumably due to charge transfer, the mechanism of which strongly depends on whether ST-21 or S-TiO₂ can absorb excitation light. For example, in the case of the p-TC, plausible charge transfer under visible-light irradiation is only electron injection from the conduction band of g-C₃N₄ to the conduction band of TiO₂, resulting in improvement of charge separation. However, photocatalytic activity of p-TC was lower than that of p-g-C₃N₄. This result suggests that electron injection from g-C₃N₄ to TiO₂ does not proceed over p-TC (Fig. 5a). In contrast, a Z-scheme reaction also possibly proceeds over p-SC (Fig. 5b) in addition to

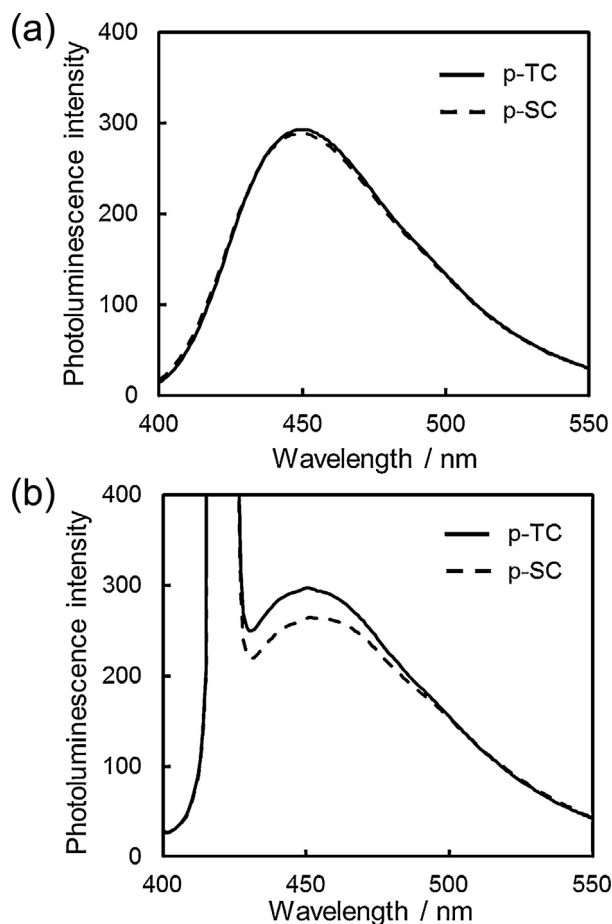


Fig. 4. PL spectra of p-TC and p-SC under excitation at the wavelength of (a) 350 nm and (b) 420 nm.

the above charge separation. The smaller PL peak intensity of p-SC than that of p-TC and the lower photocatalytic activity of p-TC indicate that Z-scheme model was main charge transfer path over p-SC rather than the charge separation model. As a result, p-SC can possess both ability for oxidation of S-TiO₂ and ability for reduction of g-C₃N₄. p-SC showed smallest R_{PL} among the prepared samples, and correlation between R_{PL} and photocatalytic activity was found (Table 1). This indicates that photocatalytic activity strongly

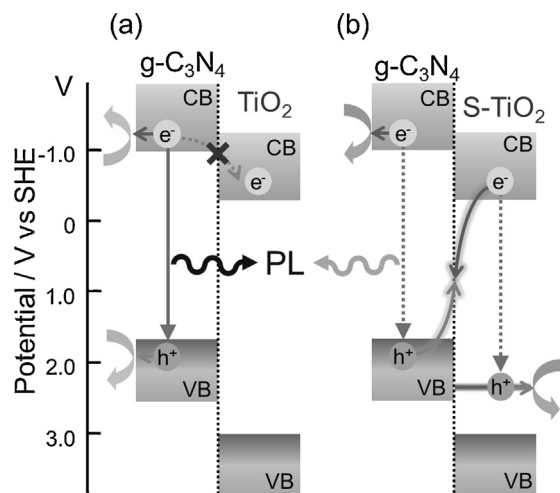


Fig. 5. Schematic images of photocatalytic reaction and PL emission of (a) p-TC and (b) p-SC under visible-light irradiation.

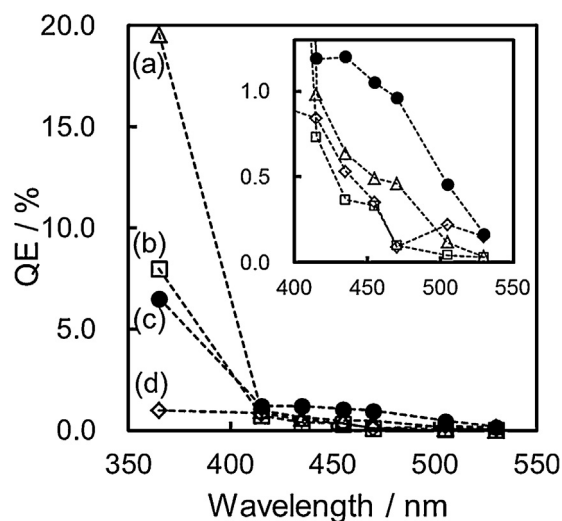


Fig. 6. Action spectra for the decomposition of acetaldehyde using (a) p-S-TiO₂, (b) p-TC, (c) p-SC and (d) p-g-C₃N₄.

depended on Z-scheme charge transfer and that a large number of contact points are important for efficient charge transfer.

3.4. Action spectra analysis

Action spectra analysis is useful for understanding a photocatalytic mechanism, especially when using a hybrid photocatalyst prepared from two kinds of semiconductors. Fig. 6 shows action spectra for the decomposition of acetaldehyde using p-g-C₃N₄, p-S-TiO₂, p-SC and p-TC. Although the hybrid photocatalysts showed lower apparent QE at excitation of 365 nm, p-SC showed higher apparent QE in the visible-light irradiation, compared to only p-S-TiO₂. Moreover, onset wavelength of the action spectrum of p-SC agreed with the absorption edge of S-TiO₂ (ca. 505 nm), indicating that photoexcitation of both semiconductors was required for a high photocatalytic activity in the visible-light region. This result confirms that Z-scheme reaction proceeds over p-SC because the photoresponses for a Z-scheme photocatalyst were dominated by absorption of the semiconductor having a wider bandgap [21].

3.5. Stability test

g-C₃N₄ included in the hybrid photocatalysts may be decomposed by photogenerated holes in the hybrid photocatalysts

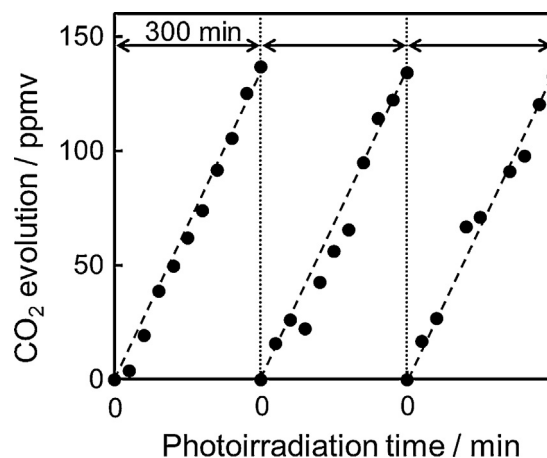


Fig. 7. Recycling reactions for photocatalytic decomposition of acetaldehyde using p-SC.

because nonoxide-type photocatalysts are less stable than metal-oxides photocatalysts [22,23]. In order to ensure stability of the hybrid photocatalyst, recycling reactions for the decomposition of acetaldehyde using p-SC were carried out. Fig. 7 shows time courses of CO₂ evolution for acetaldehyde decomposition using p-SC for 300 min of visible-light irradiation. After three recycling reactions, severe reduction of photocatalytic activity was not observed. Therefore, it was found that degradation in performance of p-SC was very small and that a high activity was maintained after several photocatalytic reactions.

4. Conclusions

A highly active photocatalyst under visible-light irradiation for organic decomposition was prepared by hybridization with g-C₃N₄ and S-TiO₂ using a planetary mill. Planetary mill treatment could increase S_{BET} and the number of contact points for charge transfer between the two semiconductors. PL measurements and action spectra analysis revealed that Z-scheme charge transfer occurred over p-SC under visible-light irradiation and that p-SC can utilize both its ability for high oxidation of S-TiO₂ and its ability for reduction of g-C₃N₄.

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